SCIENCE FOR CERAMIC PRODUCTION

UDC 666.3.015:666.365:666.766

FORMATION OF COMPOSITE STRUCTURE IN ALUMOSILICATE SYSTEMS WITH THE INTRODUCTION OF POTASSIUM TITANATES

E. Sanchez-Valdes,[2] A. V. Gorokhovskii,[1,3] N. N. Scherbakova,[1] and J. L. Rodriguez-Galicia[2]

Translated from *Steklo i Keramika*, No. 6, pp. 7 – 10, June, 2010.

The pattern of structure formation in composite ceramic materials with reaction calcination of green mixtures, including mixtures of powders of conventional alumosilicate green materials (kaolinite) and nanosize synthetic precursor materials (potassium polytitanate), is investigated. It is shown that in the course of sintering chemical interaction occurs between the components and is accompanied by the amorphization of the green mixtures and subsequent crystallization of the amorphous phase obtained with a complicated chemical composition. The phase composition of the composites obtained includes rutile, mullite, leuzit, kalsilite, and a glass phase all in different ratios, making it possible to attain high performance characteristics.

Key words: alumosilicate system, introduction of potassium titanates, nanostructure, operating characteristics.

Impregnation of a refractory by metal during service is accompanied by, aside from other chemical and thermal degradation, an increase of the thermal conductivity. For this reason, a very promising refractory material for nonferrous metallurgy is ceramic based on potassium titanates, which metal (including aluminum) melts practically do not wet.

A structured heat-insulating material using potassium titanate was proposed back in 1971 by De Soto, Inc (USA) [1]. The material was obtained during calcination of mixtures of mineral or ceramic fiber of potassium titanate and a binder based on colloidal silica; its thermal conductivity was 0.013 W/(cm · K) are 540°C and reflection coefficient for thermal radiation 75 – 80% (relative to MgO, taken as 100%).

In 1994 the companies Taiyo Kemikaru Kk, Otsuka Kagaku Kk, and Nippon Uisukaa Kk (Japan) developed a light-weight heat-insulating material [2], obtained by drying mixtures based on K_2TiO_3 nanofibers and mineral alumosilicate fibers, dispersed in a water suspension of clayey material. There are also other types of refractory and ceramic heat-insulating materials made using ready-made potassium titanate fibers.

Other promising refractory materials are ceramic materials based on aluminum titanate (tialite). Al_2TiO_5 is highly resistant to thermal shock because of its low CLTE (15×10^{-7} K^{-1}) as well as low thermal conductivity and a high melting temperature (1860°C) [3 – 6]. However, there are a number of problems in the production of such ceramic. Cast refractories based on Al_2TiO_5 can be obtained only from melts in a very narrow temperature interval (1800 – 1860°C) and using very high rates of cooling. Al_2TiO_5 crystals, obtained by crystallization of melt and with by direct cooling of the product, are prone to crack, which greatly lowers the strength of the material obtained.

The objective of the present work is to investigate the imbedding of titanates into the structure of material with alumosilicate composition and its modification during calcination in order to obtain ceramic refractory materials containing different titanates. The methodology used in this work for obtaining such a ceramic includes investigating the kinetics and the mechanism of the chemical and phase transformations as well as structure formation in green mixtures as a function of the chemical and fraction state of the green mixtures and the calcination temperature.

Binary systems containing the conventional, for synthesis of refractory materials, components (kaolinite) and a synthetic component (potassium polytitanate), were used as the raw material for synthesis of ceramic materials. Potassium polytitanate was synthesized in accordance with the method of [7] with treatment of titanium oxide powder in a salt melt at 500°C for 2 h with the weight ratios of the components

[1] Saratov State Technical University, Saratov, Russia.
[2] CINVESTAV, Saltillo, Mexico.
[3] E-mail: algo54@mail.ru.

0361-7610/10/0506-0169

TABLE 1. Chemical Composition of the Kaolinite Used

Raw material component	Oxide content, wt.%						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2
Kaolinite	54.3	42.9	0.9	0.2	0.9	0.5	0.3
Potassium polytitanate	–	–	–	–	–	19.8	81.2

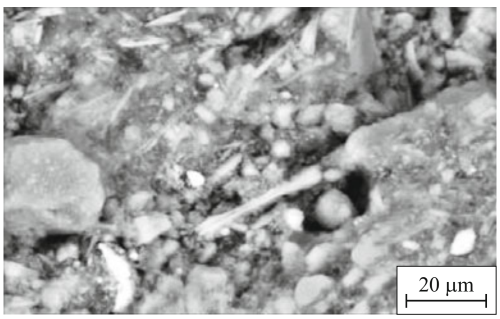

Fig. 1. Electronic photograph (× 1000) of a composite obtained at 950°C on the basis of a raw the materials mixture containing 50% potassium polytitanate.

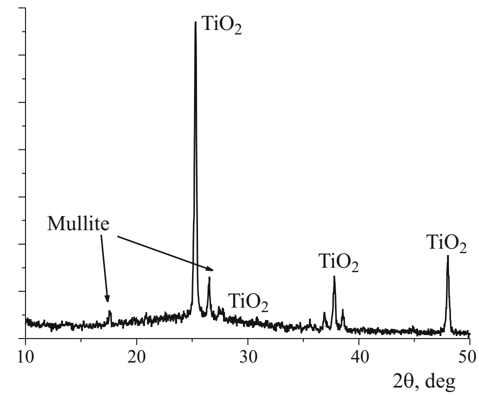

Fig. 2. Diffraction pattern of material obtained at 950°C (1 h soaking) on the basis of a raw materials mixture containing 50% potassium polytitanate.

TiO_2 : KOH : KNO_3 = 1 : 1 : 6. The chemical composition of the kaolinite used and the synthesized potassium polytitanate is presented in Table 1.

In the course of the experiment the reaction mixture of potassium polytitanate and kaolin, prepared with different component ratios, were dry pressed in a hydraulic press ("Kompakt-Alfa") under pressure 24 MPa. The ceramic blanks obtained were placed in an electric furnace. Three basic binary mixtures containing 30, 50, and 70%[4] potassium polytitanate were chosen. Considering the prospects for subsequent use of the refractory materials being synthesized at temperatures above 1100°C, reaction calcination was conducted at 950 and 1300°C for 1, 2, and 3 h.

The structure and phase composition of the ceramic samples obtained were investigated electron-probe methods of analysis using a Philips XL30ESEM scanning electron microscope, equipped with an EDAX Pegasus attachment for local x-ray microprobe analysis and a Philips X'Pert-MPD x-ray diffractometer. The JCPDS-ICDD XRD (2001) electron database was for interpretation of the diffraction patterns.

Figure 1 shows electronic photographs of ceramic samples, obtained in all three systems investigated at 950°C. Figure 2 shows the x-ray diffraction pattern of one of the samples obtained.

Calcination of the raw mixtures, prepared on the basis of binary systems of potassium polytitanate — kaolin, at 950°C results only in the initial stage of reaction synthesis. The product obtained under these conditions consists of an amorphous matrix with a complex chemical composition, formed as a result of chemical interaction of potassium polytitanate and metakaolin (amorphous product formed from kaolin at temperature above 800°C). Inclusions of crystalline phase are represented by titanium oxide (anatase, XRD-card 11-450) and mullite (XRD-card 79-1457), which are formed with partial crystallization of the initial raw materials. The amorphous matrix did not vitrify, as a result of which the strength of the samples obtained was low (20 – 30 MPa) irrespective of the ratio used for the raw materials components.

In the next experimental series calcination was performed for 1 h at 1300°C to determine the mechanism of the processes of phase formation which promote the formation of a stable glass phase in similar systems. Figure 3 shows electronic photographs of ceramic composites obtained at 1300°C, and Fig. 4 shows the x-ray diffraction patterns of the composite materials obtained.

Calcination at 1300°C in all three experimental systems is accompanied by glass formation and the formation of crystalline phases containing oxides introduced into the system with both initial components. The results obtained show that the calcination of the raw materials mixture results in intense reactive interaction of the components, accompanied by a complex system of phase transformations.

In a system containing 70% potassium polytitanate and enriched with potassium oxide, which act as a flux, the formation of a glass phase, in which rutile (TiO_2, XRD-card 3-111), leuzit ($KAlSi_2O_6$, XRD-card 71-1147), and kalsilite ($KAlSiO_4$, XRD-card 33-988) are distributed, is facilitated. As the kaolin (aluminum and silicon oxides) concentration in the system increases, ceramic composites, whose crystalline

[4] Here and below — content by weight.

TABLE 2. Kinetics of Phase Formation in the System Potassium Polytitanate — Kaolinite with Different Content of the Raw Materials Components

Potassium polytitanate content in the raw mixture, %	Phases after calcination at 1300°C with soaking time, h		
	1	2	3
30	Glass phase, rutile, leuzit	Glass phase, rutile, leuzit, kalsilite	Glass phase, rutile, leuzit, kalsilite
50	Glass phase, rutile, leuzit, tialite	Glass phase, rutile, tialite, luezit	Glass phase, rutile, tialite, luezit
70	Glass phase, rutile, leuzit, tialite	Glass phase, rutile, tialite, corundum	Glass phase, rutile, tialite, corundum

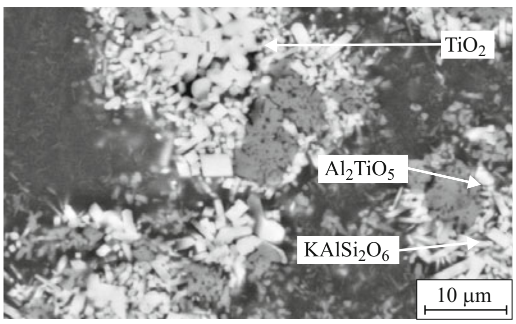

Fig. 3. Electronic photograph (× 2000) of a composite obtained at 1300°C (1 h soaking) on the basis of the materials mixture containing 50% potassium polytitanate.

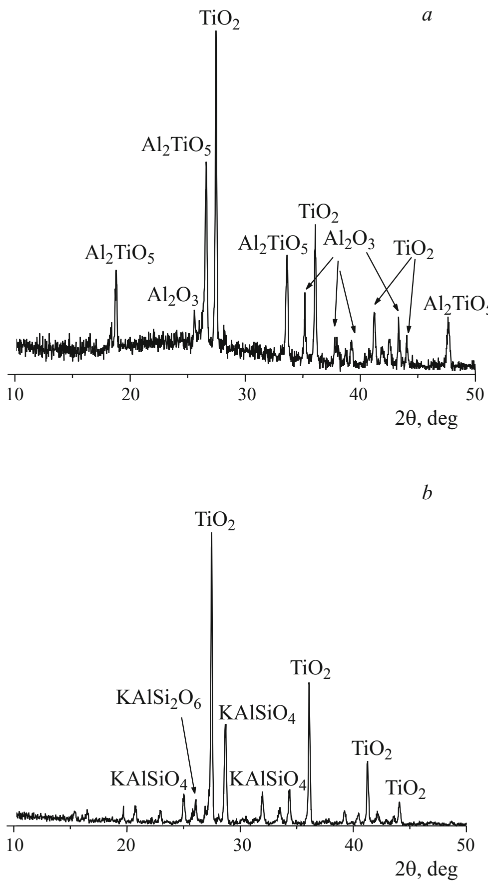

Fig. 4. Diffraction pattern of ceramic composites obtained at 1300°C (2 h soaking) on the basis of a raw materials mixture mixtures containing 30% (*a*) and 70% (*b*) potassium polytitanate.

phase is represented by rutile and tialite (Al_2TiO_5, XRD-card 81-030), are formed.

Table 2 summarizes the effect of the composition of the reaction mixture on the kinetics of phase formation in the systems studied. The phases are presented in order of their decreasing content. The results of the preliminary studies of the mechanical strength of the materials synthesized at 1300°C showed that increasing the content of potassium polytitanate in the reaction raw materials mixture results in appreciable increase of the mechanical strength of the ceramic articles; the average strength of the samples under compression (according to the results of six measurements) increases from 123 to 186 and 207 MPa, respectively.

Generalizing the data obtained, it can be concluded that in the course of reaction annealing at 1300°C there forms a melt from which during further heating the excess titanium oxide crystallized in the form of rutile while aluminum titanate (tialite) also forms in mixtures containing 50 and 30% potassium polytitanate. The formation of leuzit occurs with crystallization of melt when the melt crystallizes as the sample cools, while kalsilite crystallizes only after phase equilibrium is established in the system melt – rutile – tialite. Corundum forms only in systems with relatively low content of a silicate glass phase as a result of excess content of aluminum oxide in the system and its relatively low solubility in silicate melts.

Thus, compaction and subsequent heat treatment of the raw materials mixtures of kaolinite, conventionally used in the ceramic industry, as well as synthetic potassium polytitanate (nano-size material — precursor) result in reaction synthesis of ceramic composites, accompanied by the formation of a high-density, multiphase ceramic structure. Even though intense interaction between the components of this system starts only at temperature close to 1300°C, the phase composition of the ceramic obtained appears to be very promising.

The combination of refractory crystalline phases with very high melting temperatures (rutiel, leuzit, kalsilite, tialite), taking account of the extremely high resistance of tialite to heat shock, low values of CLTE, and wettability by aluminum melts, and taking into consideration the results of preliminary studies of the mechanical strength of the synthe-

sized ceramic composites, make it possible to conclude that this system is promising for synthesis of refractories of a new type.

REFERENCES

1. W. J. Gartner and C. T. Clark, *Patent No. 3629116 USA, C04B14/36. Compositions for Making Structured Insulating Materials*, appl. 19711221; publ. 21.12.1971.
2. T. Arai, *Patent No. 6316467 Japan, B28B1/52, Production of Incombustible Molding*, appl. 19920243987; publ. 15.11.1994.
3. M. Takahashi, M. Fukuda, H. Fukuda, and T. Yoko, "Preparation, structure and properties of thermally and mechanically improved aluminum titanate ceramics doped with alkali feldspar," *J. Amer. Ceram. Soc.*, **85**(12), 3025 – 3030 (2002).
4. H. Morishima, Z. Kato, K. Uematsu, et al., "Synthesis of aluminium titanate-mullite composite having high thermal shock resistance," *J. Mat. Sci. Lett.*, **6**(4), 389 (1987).
5. H. L. Lee, J. Y. Jeong, and H. M. Lee, "Preparation of Al_2TiO_5 from alkoxides and the effects of additives on its properties," *J. Mater. Sci.*, **32**(21), 5687 – 5695 (1997).
6. G. Rehfeld, T. Staudt, and C. Zografou, "Aluminum titanate powders — characteristics and possible applications," *Ceram. Trans.*, **1** (*Ceram. Powder Sci.*, No. 2, Pt. B), 1100 – 1107 (1988).
7. A. V. Gorokhovsky, J. I. Escalante-García, T. Sánchez-Monjarás, and C. A. Gutiérrez-Chavarría, "Synthesis of potassium polytitanate precursors by treatment of TiO_2 with molten mixtures of KNO_3 and KOH," *J. Eur. Ceram. Soc.*, **24**(13), 3541 – 3546 (2004).